F
GEOMAR
Helmholtz-Zentrum für
Ozeanforschung Kiel

Date: 15.02.2019

Cruise Report

Compiled by: Dr. Dennis Booge

F.S. Alkor **Cruise No.: AL 516**

Dates of Cruise: 12.09.2018 – 22.09.2018

Areas of Research: Physical, chemical, biological oceanography / Atmospheric chemistry

Port Calls: none

Institute: GEOMAR Helmholtz Centre for Ocean Research Kiel

Chief Scientist: Dr. Dennis Booge

Number of Scientists: 12

Projects: US NSF (title: Collaborative Research: Influence of Surfactants on Air-Sea Gas Exchange: $^{3}He/SF_6$ Experiments in the Baltic Sea)

Cruise Report

This cruise report consists of 25 pages including cover:

1. Scientific crew

Name	**Function**	**Institute**	**Leg**
Dr. Dennis Booge	Chief Scientist	GEOMAR	Entire cruise
Prof. Dr. David Ho	Scientist	University of Hawaii	Entire cruise
Dr. Toby Koffman	Scientist	Columbia University	Entire cruise
Dr. Tim Fischer	Scientist	GEOMAR	Entire cruise
James Ash	Technician	University of Hawaii	Entire cruise
Benjamin Hickman	Technician	University of Hawaii	Entire cruise
Tim Georg Steffens	Technician	GEOMAR	Entire cruise
Li Zhou	PhD Student	GEOMAR	Entire cruise
Florian-David Lange	PhD Student	University of Kiel	19.09. - 22.09.2018
Sandra Golde	Master Student	GEOMAR	Entire cruise
Melf Paulsen	Master Student	GEOMAR	Entire cruise
Theresa Barthelmeß	Master Student	GEOMAR	Entire cruise
Nhat-Thao Ton-Nu	Bachelor Student	University of Kiel	12.09. - 19.09.2018
Total	**13**		

Chief scientist:

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2. Research programme

The research programme of AL516 was identical to the previous cruise AL510 in June:
Air-sea gas exchange influences the cycling of biogeochemically important trace gases on global and regional scales (CO_2, DMS, halocarbons, and non-methane hydrocarbons), and affects water quality on local scales (e.g., oxygen exchange). Wind speed is typically used to parameterize gas transfer and, in the last few decades, advancements in field and analysis techniques have enabled us to narrow the list of reasonable wind speed/gas exchange parameterizations that are applicable in most circumstance over the ocean. However, there are environments and conditions where existing parameterizations might not be applicable. One of these environments is inland seas where surfactants might have a more dominant effect on gas exchange.
All the studies published to date that have investigated the effects of surfactants on air-sea exchange have either used artificial surface active compounds or have only measured surfactant and wave properties under natural conditions, rather than gas transfer or flux directly. This cruise, the second of two "Baltic GasEx" cruises, aimed to close that gap by conducting direct air-sea transfer measurements in the presence of natural surfactants at the Baltic Sea time series station, Boknis Eck, where natural surfactant measurements have been recorded from 2009-2014 using surface-sensitive sum-frequency generation spectroscopy. We used two different methods, simultaneously, to directly measure the gas exchange:

1) $^3He/SF_6$ tracer release experiment:

Using this technique a mixture of $^3He/SF_6$ gas is directly bubbled into the mixed layer via diffusion tubing. SF_6 and ^3He concentrations in the tracer patch will be monitored for 7-10 days following injection. As both gases have different solubilities in seawater the concentration change, as well as the ratio change over time will be used to calculate the gas transfer coefficient.

2) Trace gas eddy covariance:

The eddy covariance technique consists of computing the covariance between simultaneously measured vertical wind speed and gas concentration fluctuations at the frequencies of turbulent motion in the atmosphere (>2 Hz). This micrometeorological technique is a direct flux measurement technique. Typically, the gas measurements are made at 10 Hz and the wind measurements at 30-50 Hz. The covariance is averaged between 10 and 60 minutes. Because measurements are performed on a moving platform, the measured vertical wind speed needs to be corrected for the motion of the ship. The influence of flow distortion is omitted by using only the periods with optimal apparent wind directions (±60 degrees from the bow of the ship, (e.g., MARANDINO et al., 2007)).

In conjunction with gas exchange measurements, the abundance of surface active compounds was quantified and characterized in order to determine the influence of surfactants/microlayer on the air-sea fluxes. Furthermore, gas transfer parameterizations based on wind speed will be evaluated, both for the influence of surfactants and the difference between the open ocean and inland seas.

After injection of the tracer gas mixture, the moving patch was constantly monitored using a fully automated high-resolution SF_6 analysis system. Big CTD stations (Figure 1) were carried out twice a day in the tracer patch in order to investigate the vertical distribution of physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters. At the same time, samples for surfactants and organic matter in the surface microlayer were taken from the rubber boat. Additionally, in

between the big CTD stations, two small CTD stations were carried out in order to assess changes in the mixed layer depth. Atmospheric concentrations of CO_2 and DMS were recorded continuously at ~9 m from the sea surface from an air inlet attached to a mast at the bow of the ship.

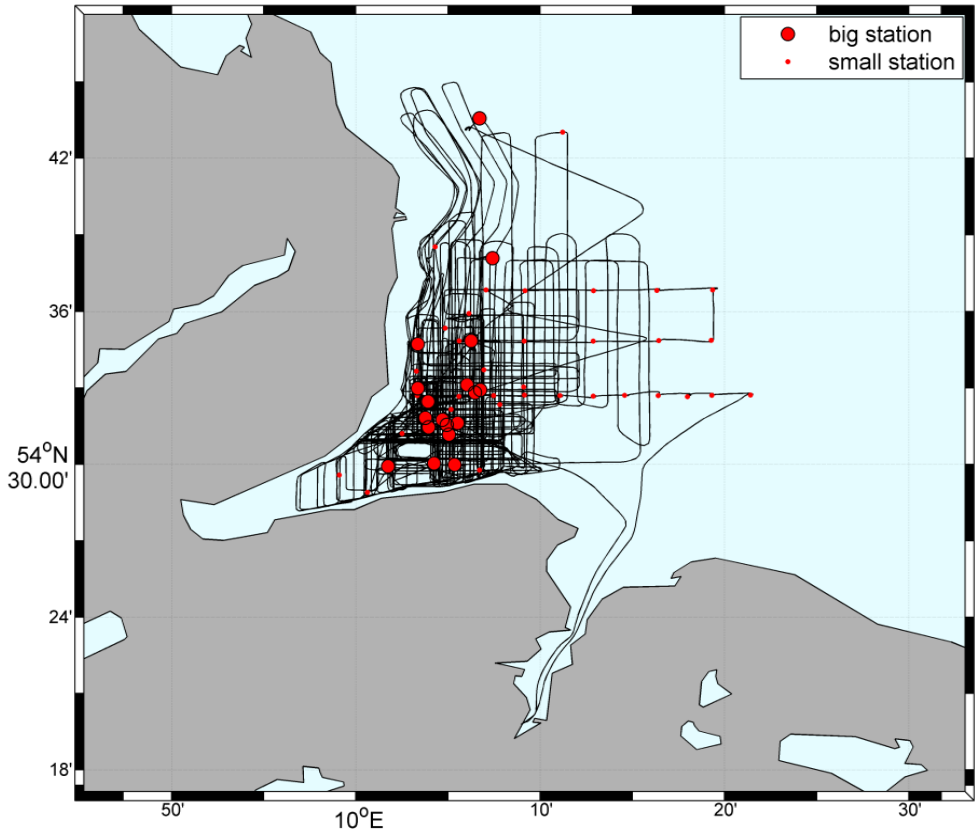

Figure 1: Cruise track of AL516 including CTD stations. Big station: CTD station including full physical, chemical and biological characterization of the water column including rubber boat samplings. Small station: CTD station without water sampling.

3. Narrative of cruise with technical details

Wednesday, 12.09.2018

The first day of the cruise was used to find the best location for injection of the tracer gas mixture. The research area was systematically mapped by performing half hourly small CTD stations in order to get information about the MLD. The ADCP of the Alkor was used to determine current directions and velocities.
During the day, continuous underway measurements monitoring the sea surface for temperature, salinity, chl-a, CDOM, SF_6 and pCO_2 were started. Furthermore, 1-3 hourly discrete sampling from the underway line for trace gases, nutrients and CDOM began.

08:00	Departure Kiel
09:36 - 19:58	20 small stations - check MLD and currents

Thursday, 13.09.2018

Continuous eddy covariance measurements for CO_2 and DMS were started.

05:59	Big station This "test" station was used to check sampling procedures and get information about the vertical distribution of chemical, physical and biological parameters.
12:17	Big station including rubber boat sampling at the determined site for tracer injection Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension), before the injection of the tracer gas mixture in order to characterize the natural background.
16:57 - 17:42	Injection of the tracer gas mixture at 54°35 N and 10°06 E

Friday, 14.09.2018

From this day on the daily working routine was mostly the same for the rest of the cruise consisting of two big stations at about 6am/4pm (duration ~ 3 hours) and two small stations at noon and midnight (duration ~ 20 min). In between those stations, the location and expansion of the tracer patch was constantly mapped using the underway SF_6 system.

06:00	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)
12:04	Small station - check MLD and currents
16:13	Big station including rubber boat sampling

Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Saturday, 15.09.2018

00:03 Small station - check MLD and currents

06:00 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:00 Small station - check MLD and currents

16:12 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Sunday, 16.09.2018

00:05 Small station - check MLD and currents

06:07 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:01 Small station - check MLD and currents

16:07 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Monday, 17.09.2018

00:04 Small station - check MLD and currents

06:01 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:07 Small station - check MLD and currents

16:08 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Tuesday, 18.09.2018

00:13 Small station - check MLD and currents

06:01 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:06 Small station - check MLD and currents

16:10 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

23:54 Small station - check MLD and currents

Wednesday, 19.09.2018

06:01 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:01 Small station - check MLD and currents

16:08 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

23:55 Small station - check MLD and currents

Thursday, 20.09.2018

06:02 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a,

nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:03 Small station - check MLD and currents

16:09 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

23:58 Small station - check MLD and currents

Friday, 21.09.2018

06:00 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:04 Small station - check MLD and currents

17:51 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Saturday, 22.09.2018

00:03 Small station - check MLD and currents

06:01 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

14:00 Arrival Kiel

4. Scientific report and first results

4.1 Hydrographic observations

CTD and salinity measurements and calibration

During AL516 57 profiles of pressure (p), temperature (T), conductivity (c) and oxygen (O) were recorded. These CTD-O2 profiles usually ranged to 1m above bottom, as recorded by the CTD-mounted altimeter (sn#453). We used the same equipment as on the companion cruise AL510 in June: a Seabird Electronics (SBE) 9plus system (IFM-GEOMAR Kiel SBE-2), attached to a 12-bottle water sampler rosette (SBE#1), and the latest Seabird Seasave software. SBE-2 had two sensor sets: p #80024, T1 #2463, c1 #2537, O1 #0215, T2 #5020, c2 #3366, O2 #2600. 60 salinity samples were taken in order to calibrate conductivity. The salinity samples are currently analyzed with an Optimare salinometer. The samples seem to contain unusual amounts of some fatty compound, which deposits on the glass of the salinometer conductivity cell. 105 oxygen samples were Winkler titrated in triplicates. Final calibrated CTD data will be available after finalizing the salinity measurements. Further a Dr Haardt fluorescence sensor (sn#14010) was attached to the rosette, but was not calibrated.

Current observations

A vessel mounted Acoustic Doppler Current Profiler (ADCP) continuously recorded current velocities. The Nortek Signature 1000 kHz transducer (a different one than on cruise AL510) was placed in the moon pool, aligned to 45 degrees. Ship heading data came via an extra GPS antenna mounted on the rear of the top deck. In combination with bottom tracking the system produced current output already corrected for possible transducer misalignment. Shortly after departure it became clear that the transducer was configured inappropriately as an uplooker, which meant that the coordinate transformation delivers current velocities which are correct in magnitude but erroneous in direction. This could not be healed by configuration changes at the deck unit, but can be corrected during post-processing. For direct readings from the screen the workaround was to mirror the apparent current vector against the ship longitudinal axis (given by the actual heading). The configuration of the Signature 1000 was 60 bins of 0.5 m, pinging at 120 per minute. The system provided enough range for the maximum 25 m depth during the cruise. The first usable bin was at 5 m depth. Apart from the complication by the wrong transducer configuration, the system worked well throughout the cruise and there were no issues with detection below the strong halocline or in oxygen depleted waters. The large issue was the ship itself interfering with the currents: during steaming the ship caused a considerable artificial current in direction to the rear of the ship, due to displacement and propulsion; during station the occasional maneuvering caused internal waves of considerable vertical amplitude. In essence, undisturbed records of the background current field could only be obtained when on station after settling of the maneuver-caused disturbances.

Microstructure measurements

A MSS90-L microstructure profiler (#028) of Sea and Sun Technology was used to infer turbulent dissipation rate and diapycnal diffusivity, aiming at quantifying diapycnal fluxes. The loosely tethered profiler was launched manually from the work boat during 17 ship stations, generally 3 microstructure profiles were performed following the procedure of near-surface gas sampling. The profiler was equipped with two airfoil shear sensors and a fast

thermistor, as well as with a pressure, a conductivity, a temperature, an oxygen and a turbidity sensor. Profiler sink velocity was adjusted to 0.65 m s^{-1}. In total 52 profiles were performed, delivering usable data usually from 2 m depth down to the bottom. During the first days of the cruise, the low wind was not able to install mixed layers beyond 5 m thickness. This is illustrated by Figure 2, which shows density stratification and mixing intensity on September 13th at 7 UTC. A diurnal warm layer seems to develop with 2.5 m thickness, the vertical exchange coefficient at its base can be estimated from measured dissipation rate and stratification as smaller than 10^{-5} m^2 s^{-1}. This means, the surface 2.5 m are near-isolated from the waters below.

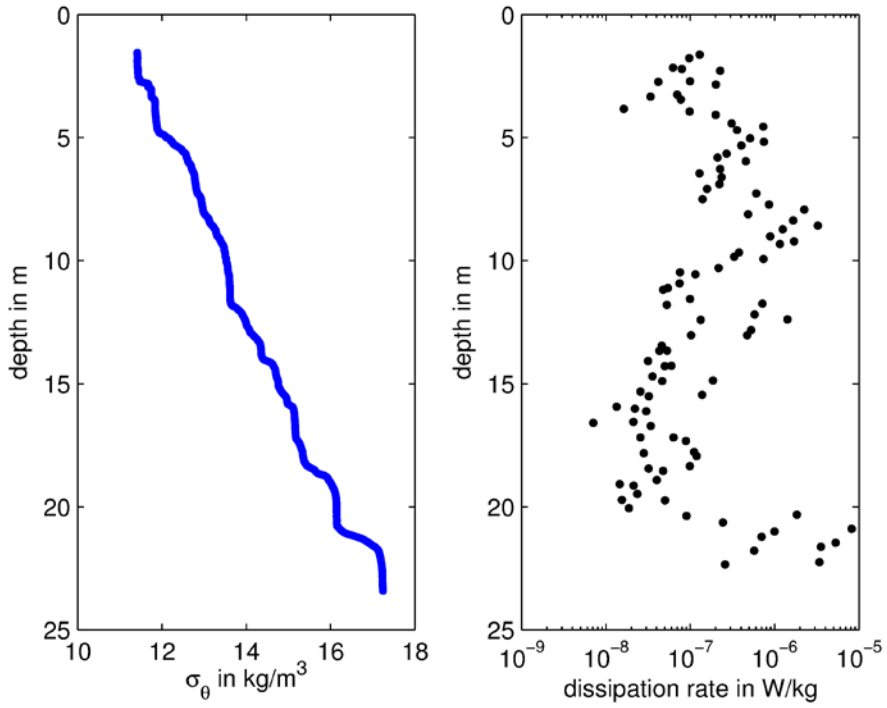

Figure 2: Depth profile of density (left) and dissipation rate (right) from microstructure sonde measurements from September 13th.

4.2 Continuous Underway pCO_2, O_2 and GTD measurements

FS Alkor's sea water pump supplied a continuous flow of surface water which was distributed through a manifold to various underway instruments (GO-pCO_2-System, flow-through (underway) box, LGR DLT-100) and bypass for discrete sampling.
Underway measurements of surface water pCO_2 were performed using a customized GO-pCO_2 measuring system (Wetbox InvNr. F076535108 with LI-6262, Drybox InvNr. F076535108, General Oceanics, Miami, FL). The instrument is described in detail in PIERROT et al. (2009). A calibration of the IR-sensor was performed approximately every five hours by using three different standard gases containing ambient air with different partial pressures of CO_2 (200, 349.8 and 449.6 ppm). The standard gases were calibrated against NOAA primary standards. After every control measurement, atmospheric pCO_2 was measured for several minutes. Therefore, air was pumped through tubing from the top of the forward mast of the ship. All temperature sensors were calibrated against international standards.
The data from the autonomous measurements of the GO-pCO_2-system started on Sep 12th 2018 at 14:50 UTC and stopped on Sep 22th 2018 at 11:55 UTC.
Underway measurements of surface water oxygen (O_2), total gas pressure (GTD) and salinity were carried out in a flow-through box and preliminary data is shown in Figure 3. The following sensors were implemented: Oxygen optodes (model 4330, SN# 1082, Aanderaa Data Instruments AS, Bergen, Norway; model CONTROS HydroFlash® O_2, SN# DO-1014-005, SN# DO-0216-004, SN# DO-0617-003, Kongsberg Maritime Contros GmbH, Kiel, Germany), GTD gas tension devices (GTD SN# 22-019-06, TDGP SN# 38-511-31, Pro Oceanus Inc., Bridgewater, Canada; turbulent water flow and mixing was ensured through an extra SBE5T pump (SN# 1041063)) and conductivity sensor (model 4319, SN# 772, Aanderaa Data Instruments AS, Bergen, Norway). Temperatures were obtained from the optodes as well as the conductivity sensor (Figure 3). The underway measurements in the flow-through box except for all three CONTROS HydroFlash® O_2 optodes were started on Sep 11th 2018 at 15:17 UTC and stopped on Sep 22th 2018 at 14:01 UTC. The running times of all three CONTROS HydroFlash® O_2 optodes is given in Table 1. The measuring interval was set to 20 seconds whereas the CONTROS HydroFlash® O2 recorded every 30 seconds.

Table 1: Running times of the different CONTROS HydroFlash® O_2 optodes in the flow-through box.

Sensor SN#	Start	Stop
DO-1014-005	Sep 13th 2018, 16:56 UTC	Sep 22nd 2018, 12:48 UTC
DO-0216-004	Sep 13th 2018, 16:56 UTC	Sep 22nd 2018, 12:44 UTC
DO-0617-003	Sep 13th 2018, 16:11 UTC	Sep 22nd 2018, 12:44 UTC

10 oxygen samples were taken from the bypass to compare, validate and partly (oxygen) calibrate these underway measurements. Oxygen samples were measured onboard using Winkler titration.

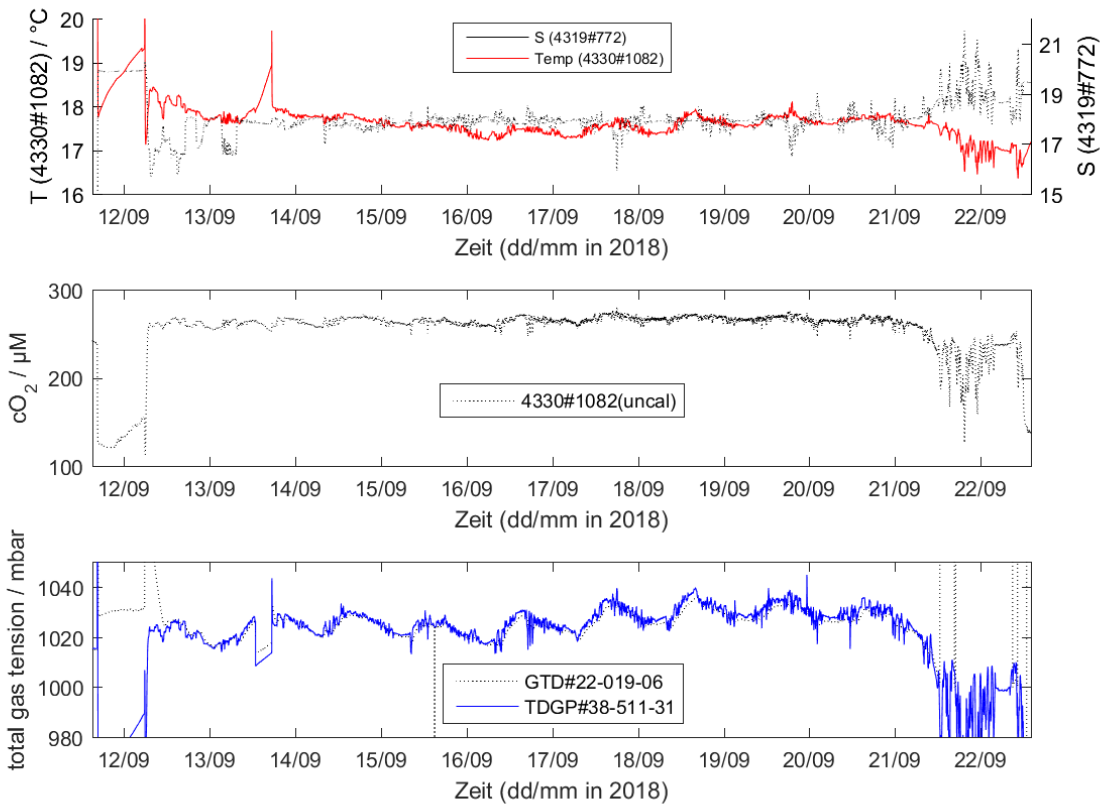

Figure 3: Preliminary (uncalibrated) results of underway temperature, salinity, oxygen and total gas tension during AL516.

4.3 ^{3}He/SF_6 tracer

After finding the best location (54°35 N and 10°06 E) for the tracer release during the first day, a gas mixture of ^{3}He and SF_6 was bubbled into the water at approximately 7 m depth on September 13th between 5 pm and 6 pm as the ship traversed three concentric hexagons with diameters of 300, 600 and 900 m.

Underway measurements of surface water SF_6 were made in order to locate the center of the tracer patch for the 6:00 and 16:00 CTD stations (Figure 4). The measurements were made on the water pumped from the ship's uncontaminated seawater intake using a continuous SF_6 system described in HO et al. (2002) and CAPLOW et al. (2004). The measurement interval was ca. 50 s.

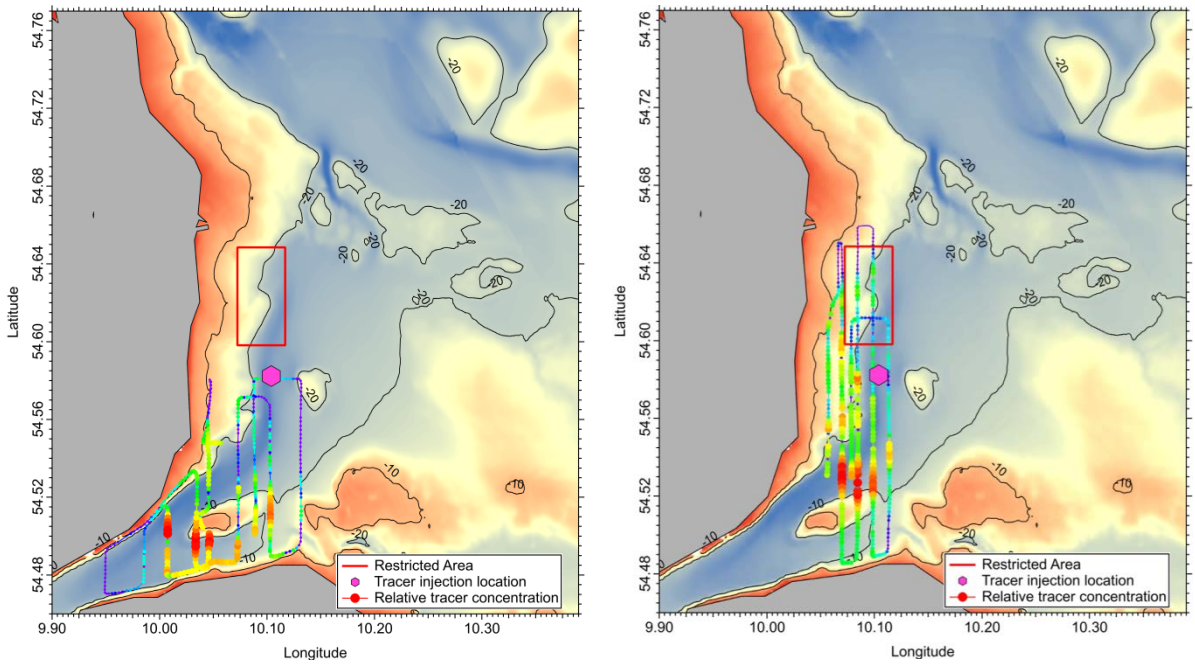

Figure 4: Two examples of underway SF_6 surveys (6am to 4pm) during AL516 on September 16th (left) and September 18th (right), respectively. Background shading is bathymetry.

At each 6:00 and 16:00 CTD station, discrete ^{3}He and SF_6 samples were taken at 7 depths to determine gas transfer velocities during the cruise. The ^{3}He samples were taken in cooper tubes (nominal volume of 40 mL) mounted in aluminum channels with stainless steel clamps, and SF_6 were taken in 550 mL borosilicate glass bottles with ground glass stoppers. The SF_6 samples were measured onboard the ship using a purge-and-trap gas chromatographic system, and the ^{3}He samples were shipped back to the laboratory for extraction and future analysis on a helium mass spectrometer.

Spreading oil

A spreading oil technique was performed to infer the presence of surfactants. Fifteen solutions of paraffin wax, each with varying concentrations of dodecanol, were used to make qualitative in situ surface tension measurements of seawater during each rubber boat station. The goal of the oil drop measurements was to determine in a qualitative sense the surface tension of seawater, which is a function of surfactant concentrations. Each solution was calibrated to spread at a particular surface tension. By placing a drop of each oil solution onto the water surface, watching to see which droplets spread or do not spread, the surface tension of the seawater can be bracketed between two discrete values roughly 1 mN m^{-1} apart. The measured surface tension range was constant from 72.9 to 73.9 mN m^{-1}, and was never out of range of the predicted surface tension (Figure 5) indicating surfactants had little effect on the surface tension of the seawater for the duration of the cruise.

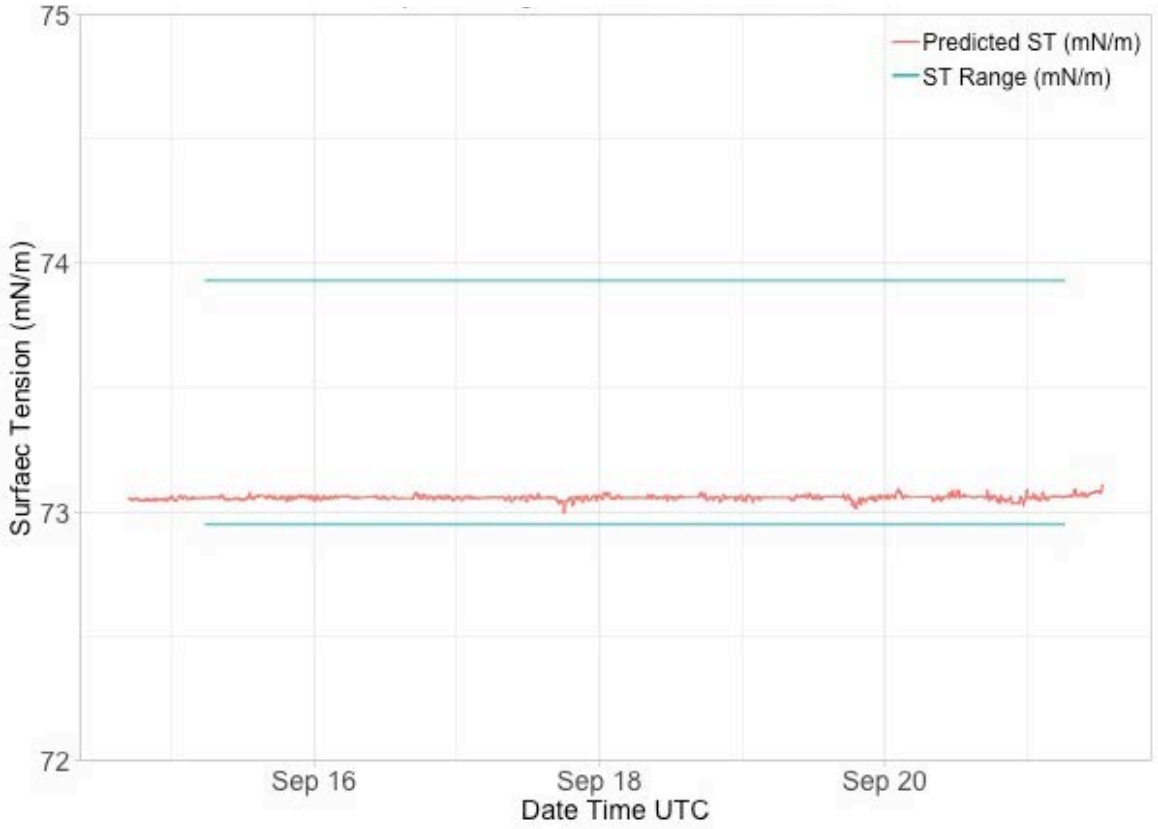

Figure 5: Predicted sea surface tension (red line) determined from measured sea surface salinity and temperature against the *in situ* surface tension measurements from the spreading oil method.

Underway SF6 measurements with an unattended, GC-based analyzer

Dissolved gases were sampled from a continuous seawater stream distributed by the system in RV Alkor's General Purpose (dry) Laboratory. A proportional valve mounted on one port of the manifold was used to roughly set a secondary flow of approximately 1.2 L min^{-1}. This flow was filtered with a 5 µm cartridge filter and delivered to a Liquicel (3M) membrane contactor which serves as a rapid gas exchange device/equilibrator. A helium 5.0 grade compressed gas (flow rate of approximately 45 mL min^{-1}) was used as a sweep gas. Water vapor-laden effluent from the membrane contactor was delivered to the analytical system described below.

Dissolved gases were analyzed using a novel, underway gas chromatograph developed at the Canada Excellence Research Chair (CERC) in Ocean Science & Technology Laboratory at Dalhousie University. Known volumes (ranging from 25 µL to 1000 µL) of carrier, standard and sample gas were introduced into the analytical circuitry via a standard 10-port, two-position valve and sample loop arrangement. The detector used during this cruise was a pulsed-discharge detector operated in electron capture (ECD) mode (Vici Valco Instruments Inc.) and was operated at 50 degrees C. The system is fully automated. A LabVIEW software application controlling the system allows the analyst to specify the frequency of blanks, standards, and samples.

Data acquisition ran continuously for the duration of the cruise. Individual samples were acquired with an approximate sampling period of 3 min. Blanks and standards were always adjacent to / separated by samples. The total number of observations during AL516 was 4835 from 2018/09/12 01:19:16 to 2018/09/22 12:46:06 UTC. This total includes samples, standards and blanks. For every 60 samples, 4 standards (2 high, 2 low) and 2 blanks were performed. Standards and blank analyses were always bracketed by samples to avoid gaps in the data. Peaks corresponding to SF_6 were observed as evidenced by consistent matching of retention time with known SF_6 standards. Peaks corresponding to other volatile tracers were observed. These compounds have yet to be identified.

Peaks deemed to be of good quality, meeting an agreed upon standard signal to noise ratio threshold are integrated with a custom data processing script implemented in Matlab. Retention times exhibiting strong peaks observed in the sample yet absent from the standard could not be identified on cruise. Subsequent analyses and validation experiments will be carried out to identify these compounds. For the retention times exhibiting peaks which are present both in the sample and standard, peak areas will be compared directly.

4.3 Air-sea gas exchange measurements

Direct gas flux measurements

During the cruise, CO_2 and DMS gas flux measurements where conducted using the eddy covariance method. Therefore, a mast was set up on the bow of the ship equipped a CSAT-3 sonic anemometer to measure three dimensional wind speed, an inertial motion unit/GPS to determine the ship's motion, and inlets for gas sampling (Figure 6). Air was pumped from the mast through tubing to the measurement systems (CO_2: LI-7200, DMS: AP-CIMS). Data processing is ongoing.

Figure 6: Mast including sensors and air inlet at the bow of the Alkor.

Indirect gas flux measurements

In order to calculate air gas exchange of DMS and isoprene indirectly, marine and atmospheric DMS concentrations were recorded. The DMS atmospheric data were recorded by a continuously running atmospheric pressure chemical ionization mass spectrometer (APCI-MS). Atmospheric DMS and isoprene were sampled from the bow mast at 10 m height and 50 m of ½'' OD Teflon tubing at 48 L min^{-1} STP. Preliminary DMS hourly mean mixing ratios range from 23.29 to 70.13 ppt (Figure 7). The average is 38.68±10.74 ppt. The concentrations change periodically over the course of the day and are usually higher at noon than at night. Preliminary isoprene mixing ratios range from 105.28 to 340.73 ppt (mean: 182.55±63.38 ppt) and do not show a diurnal cycle (Figure 7).

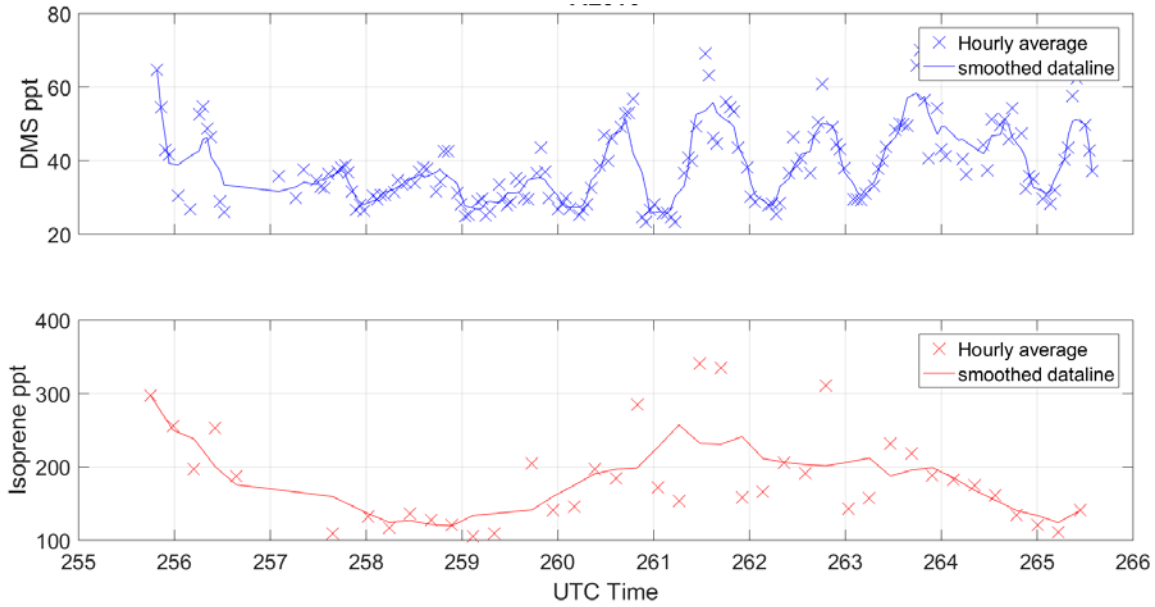

Figure 7: Time series of hourly mean atmospheric DMS and isoprene mixing ratios during AL516.

Discrete samples for DMS and isoprene were taken hourly from the underway system (inlet: ~2 m depth) and measured using a purge and trap system connected to a gas chromatograph equipped with mass spectrometer for detection. The preliminary results in Figure 8 show a diurnal cycle of CS_2 and DMS concentrations in the surface ocean, at which the diurnal cycle is more pronounced in DMS concentrations. In contrast, surface isoprene concentrations did not show a diurnal cycle and varied between 35 and 95 pmol L^{-1}.
During each big station, samples were taken from 6 different depths (3 samples within the MLD, 2 samples in the pycnocline, 1 sample below the pycnocline) in order to investigate the vertical distribution. Additionally near surface samples were taken from the rubber boat at each big station from 1 m, 50 cm and 10 cm depth as well as one sample from the SML.

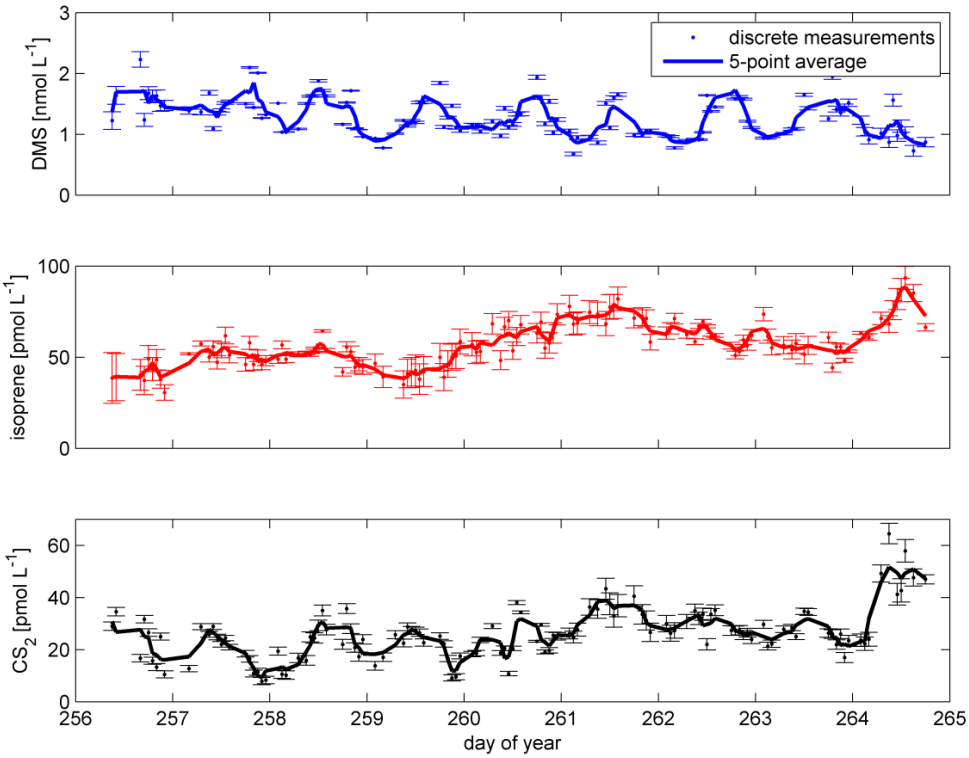

Figure 8: Hourly underway measurements of DMS, isoprene and CS_2 during AL516.

4.4 Biogenic characterization of the sea surface microlayer

During the Alkor expedition in September 2018 (AL516) the sea surface mircrolayer (SML) was monitored covering 19 stations in total. Sample collection was conducted twice a day in the morning and the afternoon applying the glass plate technique introduced by HARVEY and BURZELL (1972). The hydrophilic glass plate is immersed into the water and withdrawn carefully perpendicular to the surface. Surface tension ensures that the uppermost water layer is collected only, allowing a resolution of the SML of approximately 200 µm in depth. Reference samples were sampled at a depth of 20 cm, referred to as the underlying water (ULW). The SML is known to show enrichment of several biogenic substances along with a distinct colonization by microorganisms. This could have a potential influence on ocean atmosphere exchange processes i.e. gas exchange rates and which was also the subject of investigation. Surface activity, as a proxy for substances exhibiting non-polar behavior and thus enrich in the SML, was measured by the voltammetric approach after ĆOSOVIĆ and VOJVODIĆ (1998).

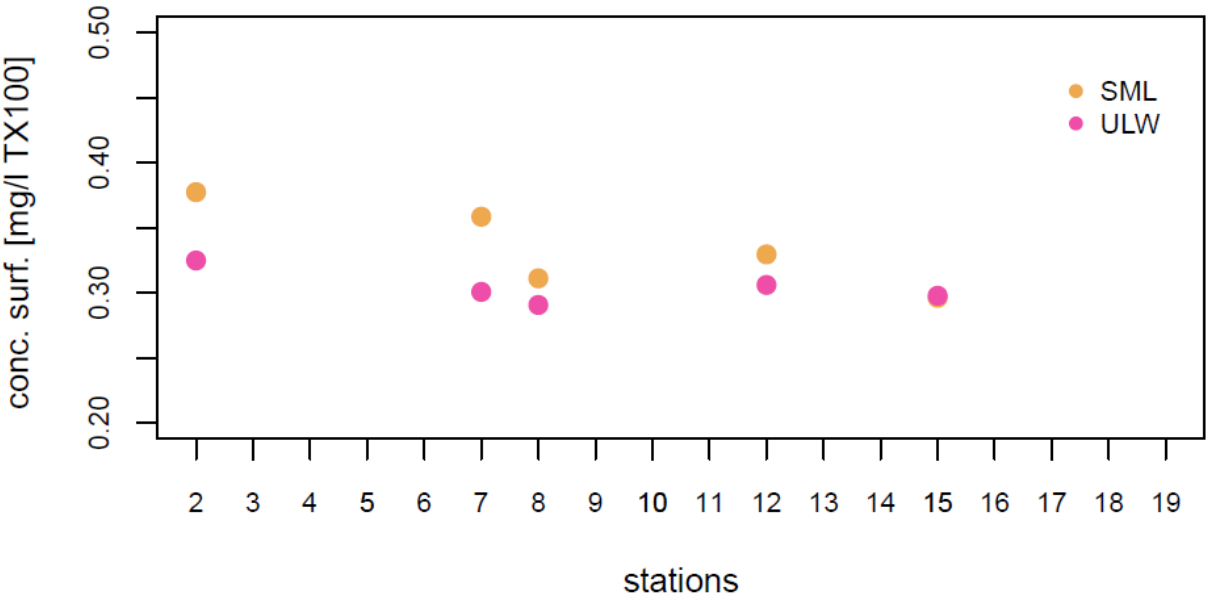

Figure 9: Surface active substances enriched in the sea surface microlayer (orange). Samples from the SML were taken by withdrawing a hydrophilic glass plate perpendicular to the water surface. Subsequently, the attached SML was whipped off. Surfactants were enriched in the SML.

Surface activity is quantified and expressed as equivalents of Triton X-100, an artificial surfactant. Only some exemplary data were evaluated until now, not allowing any final conclusions (Figure 9) although the mean concentration of surfactants does not seem to deviate from the concentration measured during the previous cruise in June (AL510). Again surfactant concentration in the SML is enriched in comparison to the ULW.
Preliminary data exist for dissolved organic carbon (DOC) contributing to the total organic carbon pool (Figure 10). Interestingly, a diurnal cycle in DOC concentration is visible with elevated concentration occurring in the afternoon. Unexpectedly, on almost every station the SML was depleted in DOC compared to the ULW.

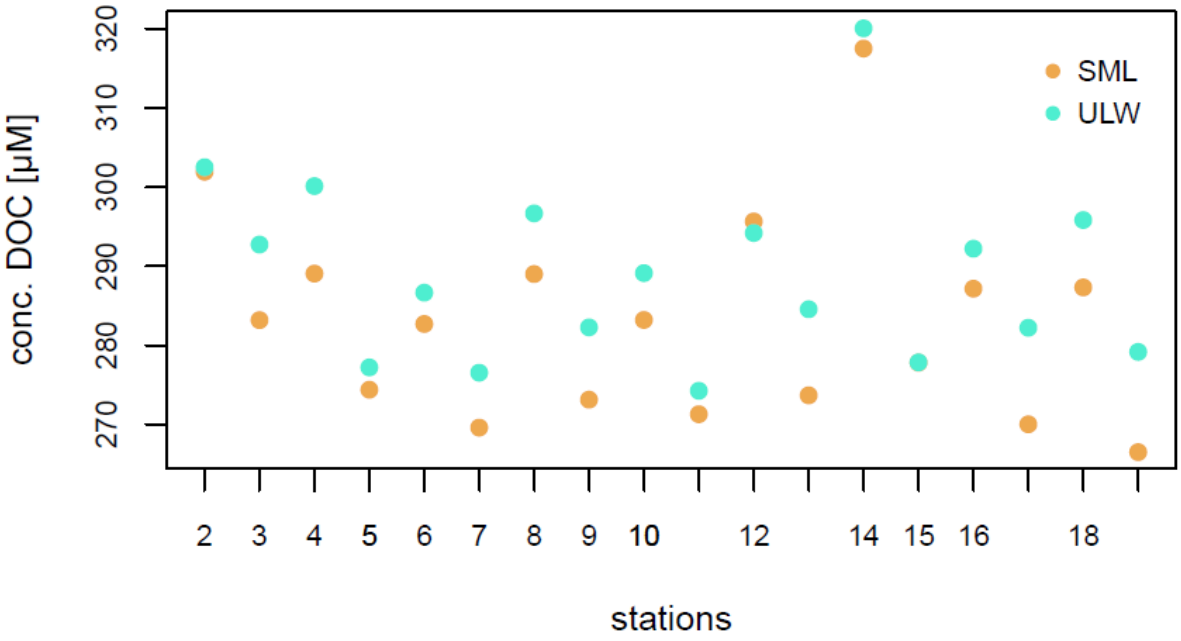

Figure 10: Dissolved organic carbon exhibiting a clear diurnal cycle during the whole cruise. DOC was depleted in the SML.

Pico- and nano-phytoplankton cells exhibited an increase in abundances in the first week of the cruise, then peaked at station 13, in the morning of the 19th of September, to subsequently decline within only three days (Figure 11).

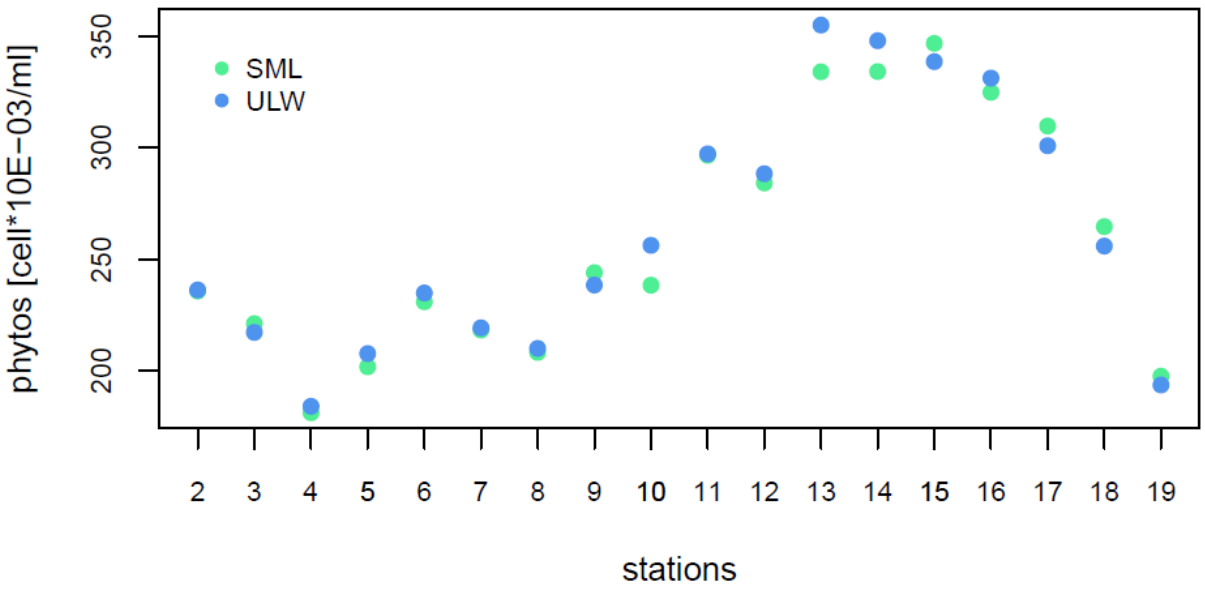

Figure 11: Pico- and nano phytoplankton abundances analyzed by flow-cytometry. Cell numbers within the ULW frequently exceeded concentrations in the SML.

The highest concentration of DOC coincided with the maximum in phytoplankton abundances. Bacterial numbers increased in the first five days and reached their peak at station 9 and 10, at the 17th of September (Figure 12). Bacterial numbers ranged from 1.4 up to 2.8 10^6 cells mL^{-1} which is comparable to abundances observed in June. However, in the end of the AL510 cruise, phytoplankton abundance ranged from 40 up to 150 10^3 cells mL^{-1} and thus show substantially lower abundances in September when pico- and nano-sized phytoplankton ranged roughly between 180 and 350 10^3 cells mL^{-1}.

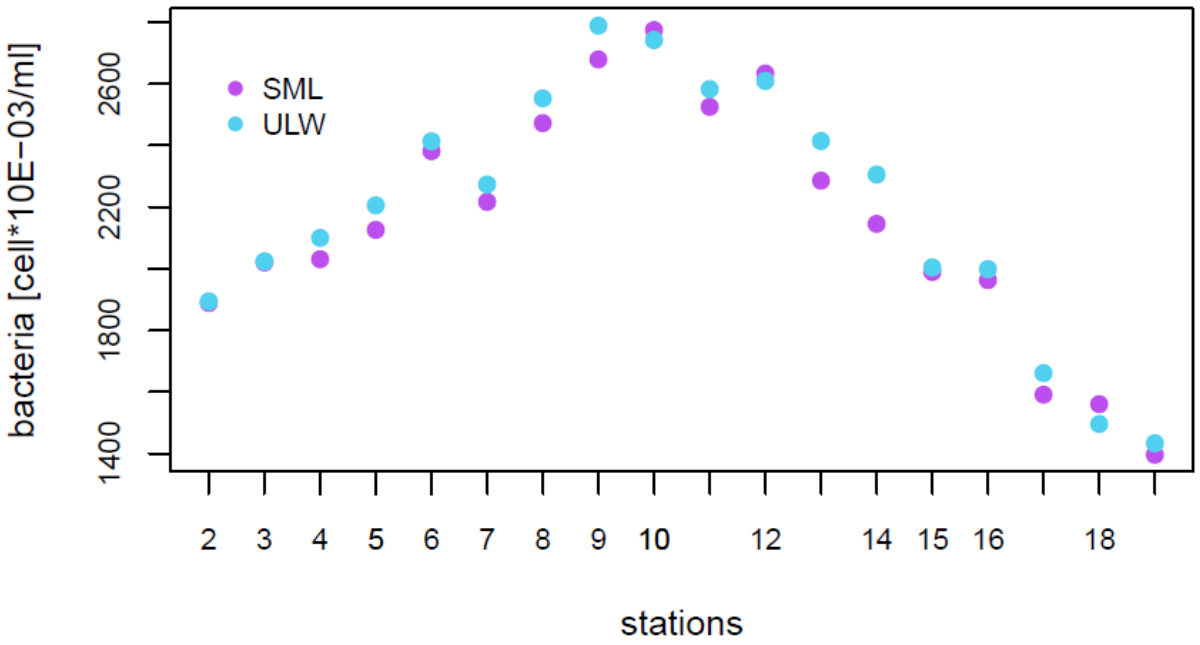

Figure 12: Bacterial abundances evaluated by flow-cytometry. Cell numbers within the ULW normally exceeded the concentration found in the SML.

4.5 Physical and chemical characterization of the sea surface microlayer

Lab-based analysis of the surfactant state of the sea surface microlayer (SML) has been performed by different analytical techniques including Vibrational Sum Frequency Generation Spectroscopy (VSFG, parameter: surfactant spectral intensity), tensiometry (parameter: surface tension), and Langmuir trough (LT) compression isotherms (parameter: surface pressure). These measurements complement the data on surfactant activity determined by phase sensitive AC voltammetry. During all rubber boat stations, SML samples have been collected both by the glass plate (triplicates) and the Garret screen (duplicates) sampling techniques (CUNLIFFE and WURL, 2014). Garret screen samples (duplicates) were also collected directly from the ship and bulk water samples were taken from the CTD casts at a depth of typically 18-25 m. Additional SML samples have been collected for later quantification of 3-hydroxy fatty acids using a LC/ESI/Orbitrap-MS setup at TROPOS (Manuela van Pinxteren, Leibniz Institute for Tropospheric Research, Leipzig, Germany). 3-hydroxy fatty acids have been suggested as biomarkers of endotoxins and Gram-negative bacterial community (LEE et al., 2004).

Vibrational Sum Frequency Generation

VSFG is a non-linear surface-sensitive laser spectroscopic technique used to probe vibrations of molecules located directly at the air-sea water interface (LAß and FRIEDRICHS, 2011). VSFG spectra have been recorded using a 532 nm up-conversion picosecond scanning type spectrometer (EKSPLA, Lithuania). In the context of SML analysis, VSFG can be used to detect organic surface active molecules (surfactants).

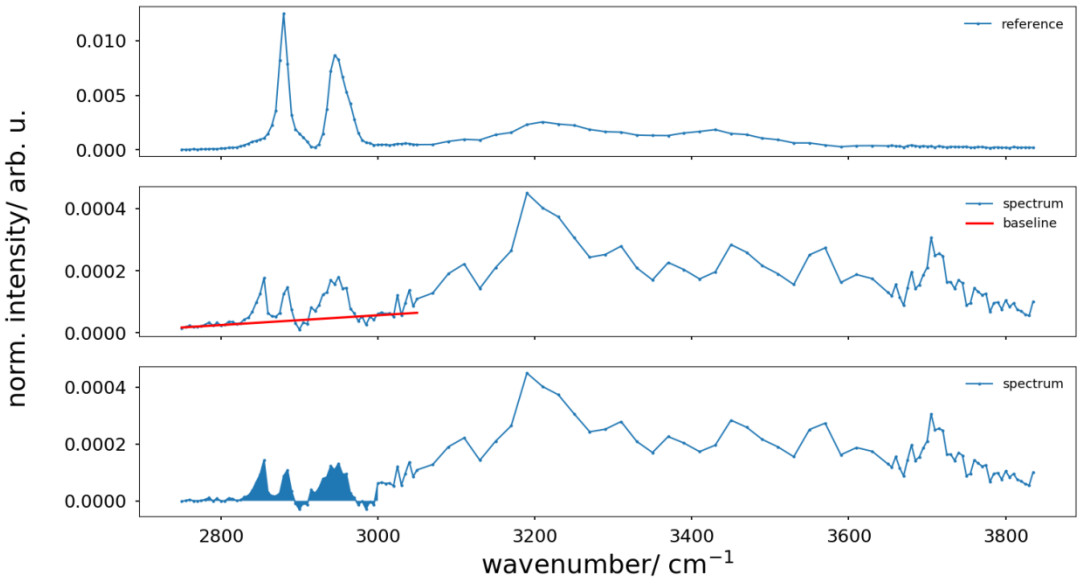

Figure 13: VSFG analysis of a typical SML sample: DPPC reference spectrum, baseline correction and integration of the CH region of the spectrum.

Figure 13 illustrates a typical sample analysis yielding a surface coverage of 13%. As the overall signal intensities turned out to be rather weak for the SML samples, a proper baseline subtraction was necessary, which has been implemented by an automatic Python analysis routine. The preliminary data analysis of all samples shown in Figure 14 reveals that during

both cruises (AL510 and AL516) the average surface coverage was low (< 10%) and close to the detection limit of the method. However, SML samples yield higher signals than bulk water samples, consistent with an enrichment of surfactants in the SML.

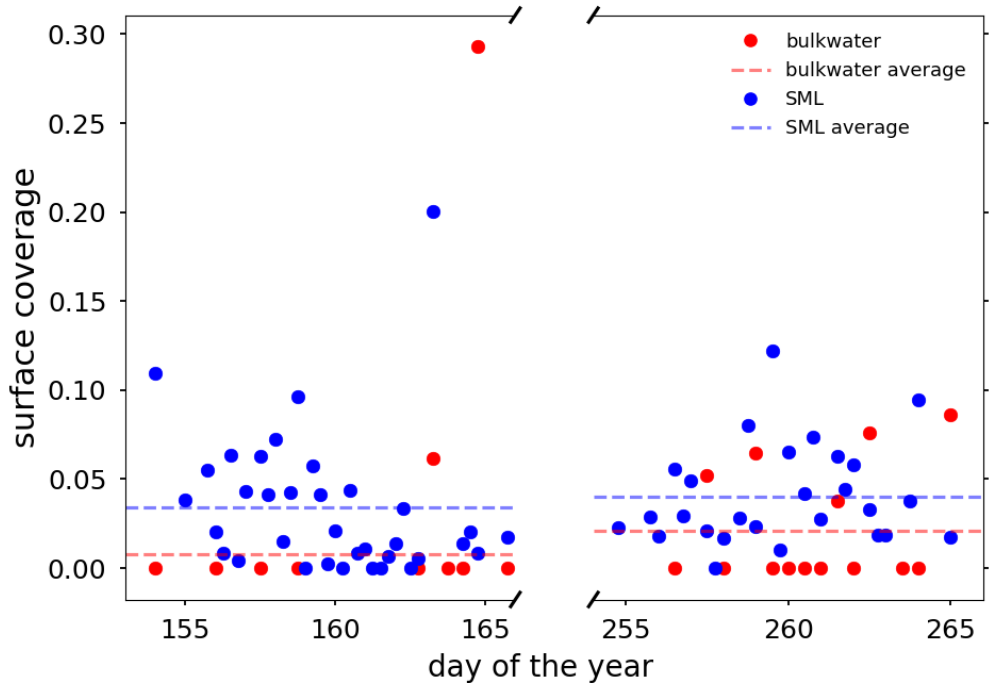

Figure 14: Surface coverage values detected from SFG analysis.

Tensiometry

Surfaces tension σ was measured by a Du-Noüy-type precision tensiometer (AquaPi Plus, Kibron, Finland) at room temperature (21 °C) with an accuracy of ±0.2 mN m^{-1}. The data in

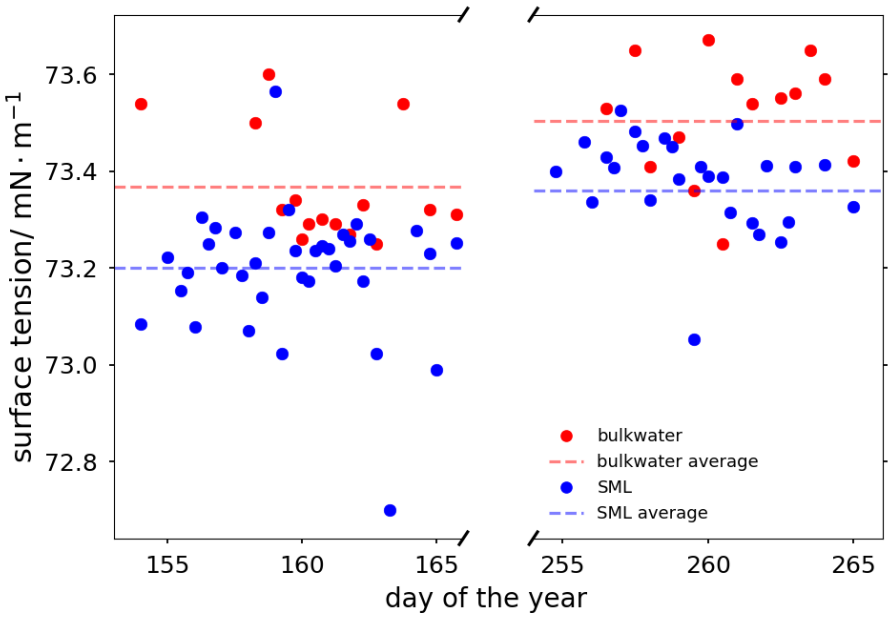

Figure 15: Average surface tension values (not yet corrected for salinity).

Figure 15 reveal values between 72.7 and 73.6 mN m^{-1}, which is close to the expected values of 73.2 ±0.3 mN m^{-1} for a clean water surface at salinity S = 19.5. The identified preliminary trends are: surface tensions are slightly lower for the SML samples compared to the bulk water and surface tensions are slightly higher for the second cruise. However, note that the observed trends are close to the accuracy of the measurements and still need to be corrected for salinity effects.

Langmuir Trough

Surface pressure isotherms were measured in a Langmuir trough (RK1, Riegler & Kirstein, Germany) by monitoring the surface pressure with a Wilhelmy balance as a function of the surface area with a precision of ±0.8 mN m^{-1}. The total compression ratio of the area A, $r=A_{start}/A_{end}$ which was achieved by moving Teflon barriers, was r=6.3. The surface pressure at maximum compression was taken as a measure for surfactant abundance. The data in Figure 16 indicate slightly higher surfactant abundance for the first cruise. The overall lower value for the bulk water samples is consistent with surfactant enrichment in the SML.

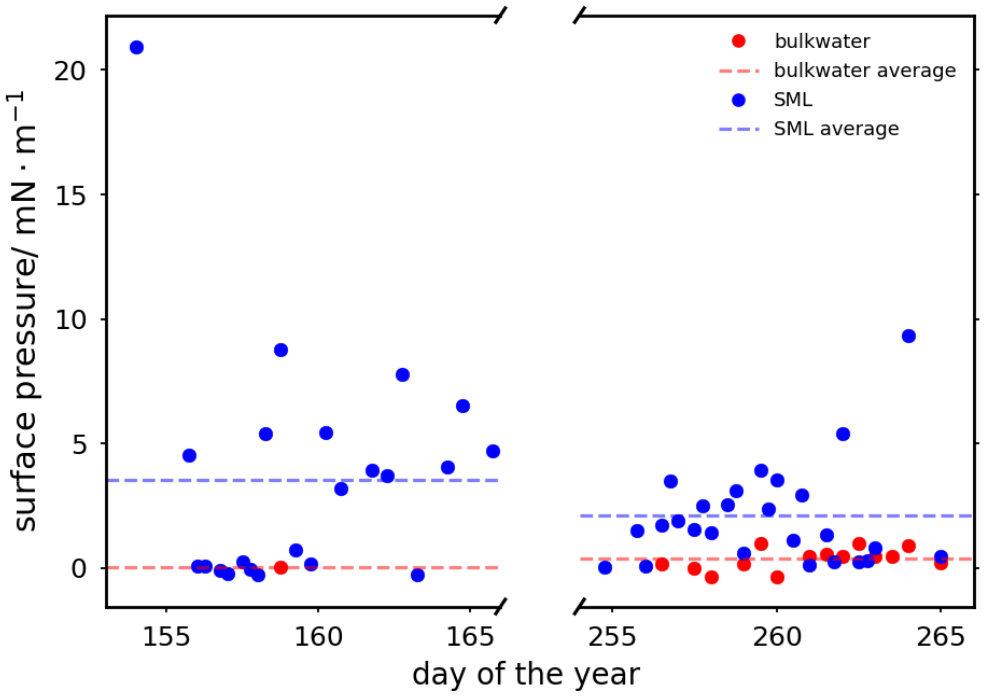

Figure 16: Average maximum surface pressure from Langmuir trough analysis.

5. Scientific equipment: instruments deployed into the water

- Microstructure sonde
- Moving CTD for tracer deployment
- CTD Seabird Electronics attached to a 12-bottle water sampler rosette
- Nortek Signature 1000 kHz transducer (using the ships ADCP)
- Deployment of rubber boat for glass plate and Garret screen sampling

6. Acknowledgements

Special thanks to the captain Jan Peter Lass and the entire crew of RV Alkor for their great support during AL516. The cruise was partly funded by the US NSF. We thank GEOMAR Helmholtz Centre for Ocean Research Kiel for grant EP516 and additional funding by transatlantic Helmholtz Research School for Ocean System Science and Technology (HOSST).

7. Appendices

A station list (stationsplan_AL516.xlsx) was uploaded electronically together with this report.

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